Spectral Band Absorptance of Radiation Traversing Two or More Cells in Series

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ABSTRACT

Theoretical equations are derived for the spectral band absorptance of radiation which traverses two or more cells in series. The amount of absorbing gas, pressure, and temperature of each cell may be chosen independently. Limiting expressions are obtained when the absorptance of all of the cells can be represented by either the weak line or the strong line approximation as well as when some of the cells can be represented by the weak line approximation while the remainder can be represented by the strong line approximation. Some of the results apply to any spectral band, while other results apply only to particular band models or to nonoverlapping spectral lines. The dependence of the absorptance on the various parameters is illustrated by numerous examples. The conditions for the validity of the usual interpolation procedure for obtaining the equivalent parameters for a homogeneous path are derived.

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I. Introduction

A number of laboratory measurements have been made of the absorptance of the infrared bands of atmospheric gases as a function of absorber concentration and pressure. Unfortunately it is not possible to simulate under controlled conditions in the laboratory the continually varying values of the pressure, temperature, and absorber concentration which occur along an actual slant path in the atmosphere. The only means for approximating in the laboratory the conditions along an atmospheric slant path is to allow the radiation to pass through a series of cells in series. The absorber concentration, pressure, and temperature of each of these cells may be adjusted independently to simulate the desired slant path. In addition the study of the absorptance of two or more cells in series can provide valuable additional information of the influence of absorber concentration, pressure, and temperature upon the interaction of radiation with a complex band of spectral lines.

Two different laboratory experiments[1,2] have been reported which used two cells in series, each of which contained the same absorbing gas. Because of the experimental interest in this problem, it seemed worthwhile to investigate theoretically the absorption laws for a series of cells in series. Furthermore this study provides a new understanding of the absorption laws which apply to an atmospheric slant path.[3,4]

The absorptance of a single spectral line by two or more cells in series is studied in Section II. The added complication introduced when the spectral lines overlap is discussed in Section III, where the results for the Elsasser and the statistical models are presented together with some general results applicable to any band. Finally the interpolation procedure[4,5,6,7] which has proven to be so useful for atmospheric slant paths is applied to this

problem in Section IV. It is shown to be valid only under certain specified conditions.

II. Absorptance by a Single Spectral Line

The equivalent width, W, of a single spectral line is calculated in this section when the radiation has passed through two or more cells in series. The complicating effects caused by the overlapping of the spectral lines are not considered until the next section. The equivalent width is defined as

$$W = \int_{\Delta\nu}[1-\exp(-\Sigma_j k_j u_j)]d\nu , \tag{1}$$

where $\Delta\nu$ is the frequency interval considered, k_j and u_j are the absorption coefficient and mass of absorbing gas per unit area in the jth cell through which the radiation is passing. Of course, the results can be applied to a band of nonoverlapping lines by merely multiplying W by the number of lines in the band.

The absorption coefficient for the jth cell can be written

$$k_j(\nu,p_j,T_j) = S_j(T_j)b_j(\nu,p_j), \tag{2}$$

where S_j is the line intensity, p_j and T_j are the pressure and temperature in the jth cell, and b_j is the line shape factor. For the Lorentz pressure broadened line shape, the line shape factor is

$$b_j = \alpha_j/\left\{\pi[(\nu-\nu_o)^2 + \alpha_j^2]\right\}, \tag{3}$$

where ν_o is the wavenumber of the line center and α_j is the half-width in the jth cell.

A. Weak Line Approximation

The weak line approximation is valid when the absorption of the radiation is small even at the line center. If this is the case for the radiation passing through the series of absorption cells, then the exponential in Eq. (1) can be expanded in a power series to obtain

$$W = \sum_j u_j \int_{\Delta\nu} k_j \, d\nu. \tag{4}$$

The equivalent width of radiation passing only through cell 1 is

$$W_1 = \int_{\Delta\nu} [1-\exp(-k_1 u_1)] d\nu, \tag{5}$$

or when the weak line approximation is valid we have

$$W_1 = u_1 \int_{\Delta\nu} k_1 \, d\nu. \tag{6}$$

Thus from Eqs. (4) and (6), it follows that

$$W = \sum_j W_j \tag{7}$$

The equivalent width is the sum of the equivalent widths for the radiation passing through each of the cells by itself. This result is valid for any frequency interval and any line shape. The only condition is that the weak line approximation be valid for each cell considered individually.

The weak line approximation is usually considered to mean that the first two terms are retained in the expansion of the exponential, as in the derivation of Eq. (7). For some purposes the first three terms in the expansion are needed. For simplicity, let us consider the case when two cells are in series. In this case, we obtain from Eq. (1) and the

expression for the Lorentz line shape, Eq. (3), that

$$W = W_1+W_2 - \frac{2S_1\alpha_1u_1S_2\alpha_2u_2}{\pi^2}\int_0^{\frac{1}{2}\Delta\nu}\frac{d\nu}{(\nu^2+\alpha_1^2)(\nu^2+\alpha_2^2)} , \qquad (8)$$

where the origin of the coordinates for ν has been taken at the line center. The quantities W_1 and W_2 stand for the equivalent width of the cells 1 and 2 considered individually where terms have been retained through quantities of the second order. After performing the indicated integration we obtain the result that

$$W = W_1+W_2 - \frac{2S_1u_1S_2u_2}{\pi^2(\alpha_2^2-\alpha_1^2)}\left[\alpha_2 \tan^{-1}\frac{\Delta\nu}{2\alpha_1} - \alpha_1 \tan^{-1}\frac{\Delta\nu}{2\alpha_2}\right]. \qquad (9)$$

When all of the absorption takes place within the frequency interval $\Delta\nu$, Eq. (9) reduces to the simpler form

$$W = W_1+W_2-\frac{S_1u_1S_2u_2}{\pi(\alpha_1+\alpha_2)}. \qquad (10)$$

This second order correction to the equivalent width is valid only for the Lorentz line shape. The extension of these results to the case when more than two cells are in series is immediate. The correction term in this case is merely the sum of terms with all possible combinations of the indices.

B. Strong Line Approximation

The strong line approximation is valid when the absorption of the incident radiation is virtually complete over a frequency interval at least several half-widths wide around the line center. When this is the case, the factor α_j^2 may be neglected[8,9] compared to $(\nu-\nu_o)^2$ in the expression for the Lorentz line shape factor, Eq. (3), in calculations of the amount of radiation which is absorbed.

If the strong line approximation is valid for each of the cells in series, then we obtain from Eqs. (1), (2), and (3) that

$$W = \int_{\Delta\nu} \left\{ 1-\exp\left[- \frac{\sum_j S_j \alpha_j u_j}{\pi(\nu-\nu_o)^2} \right] \right\} d\nu. \tag{11}$$

If the variable is changed to $z^2 = \sum_j S_j \alpha_j u_j / [\pi(\nu-\nu_o)^2]$, then

$$W = \frac{2[\sum_j S_j \alpha_j u_j]^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \int_{2[\sum_j S_j \alpha_j u_j]^{\frac{1}{2}}/\pi^{\frac{1}{2}}\Delta\nu}^{\infty} z^{-2}(1-e^{-z^2})dz. \tag{12}$$

Since the equivalent width W_j of the jth cell alone is

$$W_j = 2 S_j^{\frac{1}{2}} \alpha_j^{\frac{1}{2}} u_j^{\frac{1}{2}},$$

then the total equivalent width can be written as

$$W = \pi^{-\frac{1}{2}} (\sum_j W_j^2)^{\frac{1}{2}} \int_{(\sum_j W_j^2)^{\frac{1}{2}}/\pi^{\frac{1}{2}}\Delta\nu}^{\infty} z^{-2}(1-e^{-z^2})dz \tag{13}$$

or

$$W/\Delta\nu = g[(\sum_j W_j^2)^{\frac{1}{2}}/\Delta\nu], \tag{14}$$

where the definition of the function g can be obtained by a comparison of Eqs. (13) and (14).

When all of the absorption from the spectral line occurs within the interval $\Delta\nu$, then Eq. (13) reduces to (cf. Gryvnak and Shaw[1])

$$W = (\sum_j W_j^2)^{\frac{1}{2}}. \tag{15}$$

Thus the equivalent width for radiation absorbed by a series of cells is given by the square root of the sum of the squares of the individual equivalent widths of each cell. The assumption has been made in deriving this result that the strong line approximation is valid for each individual absorption cell and the Lorentz line shape is valid.

The above result can be generalized to any pressure broadened line shape which has been proposed including those with asymmetric wings.[10] If the line shape factor varies as $(\nu-\nu_o)^n$ in the far wings of the spectral line, then we find by repeating the derivation which lead to Eq. (15) that

$$W = (\sum_j W_j^n)^{\frac{1}{n}} \tag{16}$$

When it cannot be assumed that all of the absorption from the spectral line occurs within the interval $\Delta\nu$, Eq. (13) must be used. It is possible to evaluate this integral with the result that

$$W = (\sum_j W_j^2)^{\frac{1}{2}} \left\{ 1-\phi[(\sum_j W_j^2)^{\frac{1}{2}}/\pi^{\frac{1}{2}}\Delta\nu] \right\} + \Delta\nu \left\{ 1-\exp[-\sum_j W_j^2/\pi\Delta\nu^2] \right\} \tag{17}$$

where

$$\phi(x) = 2\pi^{-\frac{1}{2}} \int_o^x e^{-y^2}\, dy.$$

C. Mixture of Weak and Strong Line Approximations

When the radiation passes through a series of absorption cells, it may happen that the parameters in the first cell are such that the weak line approximation is valid for that cell considered by itself, while the strong line approximation is valid for the second cell. The equations which

apply in this important practical situation are derived in this section. For simplicity of presentation it is assumed that there are only two cells in series. These results can easily be extended to more complicated situations where there are more absorption cells.

Assume first that the absorption in the first and second cells can be described by the weak line and strong line approximations respectively. Then treating each of these approximations in the usual manner, we find from Eqs. (1), (2), and (3) that

$$W = \int_{\Delta\nu} [1-(1-k_1u_1)e^{-k_2u_2}]d\nu$$

$$= W_2 + \frac{2S_1\alpha_1u_1}{\pi}\int_o^\infty \frac{1}{\nu^2+\alpha_1^2}\exp(-\frac{S_2\alpha_2u_2}{\pi\nu^2})d\nu . \tag{18}$$

With the aid of the substitution $z = \alpha_1^2 S_2\alpha_2u_2\nu^{-2}$, we find that[11]

$$W = W_2 + W_1e^{\eta}[1-\phi(\eta^{\frac{1}{2}})], \tag{19}$$

where

$$\eta = 2\beta_1^{-2}\beta_2^2x_2 = S_2\alpha_2u_2/\pi\alpha_1^2 \tag{20}$$

$$\beta = 2\pi\alpha/d \tag{21}$$

$$x = Su/2\pi\alpha, \tag{22}$$

and the function $\phi(x)$ is defined after Eq. (17). The quantity d is the mean line spacing in a band. It has no physical meaning for a single spectral line and cancels out of the equations. It is introduced here for later use with a band. Useful forms of Eq. (19) can be obtained from the usual expansions of $\phi(\eta)$ when η is small or large compared to unity with

the result that

$$W = W_2 + W_1(1-2\pi^{-\frac{1}{2}}\eta^{\frac{1}{2}}+\eta+\ldots), \quad \eta << 1, \tag{23}$$

and

$$W = W_2 + W_1 \frac{1}{\pi^{\frac{1}{2}}\eta^{\frac{1}{2}}}(1-\frac{1}{2\eta} + \frac{3}{4\eta^2} - \ldots), \quad \eta >> 1. \tag{24}$$

The equivalent width can be obtained from Eq. (19), (23), or (24) when the first absorbing cell considered by itself interacts with the radiation according to the weak line approximation and the second cell according to the strong line approximation. In this case the equivalent width is equal to the sum of the equivalent width of the second cell and the equivalent width of the first cell multiplied by a correction factor. This correction factor is very small when $\eta >> 1$ so that the equivalent is nearly equal to W_2.

On the other hand when $\eta << 1$ the correction factor is nearly unity so that the equivalent width is nearly equal to $W_2 + W_1$. In order for η to be much less than unity, it follows from Eq. (20) that $\beta_1^2/\beta_2^2 >> x_2$. Since the second cell is assumed to be represented by the strong line approximation, it follows that $x_2 > 2$ and that therefore $\beta_1 >> \beta_2$. Thus the first cell, whose absorption considered by itself is described by the weak line approximation, makes an appreciable contribution to the total absorption when in series with cells described by the strong line approximation only when the pressure in the first cell is very much larger than that in the other cells.

When the absorption in the first cell is described by the strong line approximation and that in the second cell by the weak line approximation, a

similar derivation to that which has just been discussed shows that

$$W = W_1 + W_2 e^{\xi}[1-\phi(\xi^{\frac{1}{2}})], \tag{25}$$

where

$$\xi = 2\beta_2^{-2}\beta_1^{2}x_1. \tag{26}$$

Two useful approximations to Eq. (25) are

$$W = W_1 + W_2(1-2\pi^{-\frac{1}{2}}\xi^{\frac{1}{2}}+\xi+\ldots), \quad \xi << 1 \tag{27}$$

and

$$W = W_1 + W_2 \frac{1}{\pi^{\frac{1}{2}}\xi^{\frac{1}{2}}}(1-\frac{1}{2\xi} + \frac{3}{4\xi^2} - \ldots), \quad \xi >> 1. \tag{28}$$

D. Illustrative Examples

The functional dependence of the absorption on the various parameters is illustrated in this section for some typical cases. Let us consider as examples, the variation of the absorption when $x_1 = 0.01$, 1, and 100, so that the first absorbing cell is in the region where the absorption can be described respectively by (1) the weak line approximation, (2) a case intermediate between the weak and strong line approximation, and (3) the strong line approximation.

The equivalent width divided by $2\pi\alpha_1$ as a function of $1 + (\beta_2 x_2/\beta_1 x_1)$ is shown in Fig. 1 when $x_1 = 0.01$. The uppermost limiting curve which is a straight line on a log-log plot is the equivalent width when the absorption in both cells can be described by the weak line approximation. All of the curves for the actual equivalent width as shown in the figures of this article were calculated by numerical evaluation of Eqs. (1), (2), and (3) on an electronic computor. The results were checked against the approximate

expressions derived in Section II, A-C. These approximate expressions are compared with the exact results in more detail in Section IV.

The curves in Fig. 1 are for various constant values of $q = \beta_2/\beta_1$. Since the value $x_1 = 0.01$ is fixed, the abcissa is proportional to 1 + (constant)u_2 along a given curve for constant q. For a fixed value of u_2 as the ratio q increases, the equivalent width also increases until the weak line limit is approached. As u_2 increases for a fixed value of q, the equivalent width is given first by the limiting weak line curve until qx_2/x_1 is approximately 20q. Then the equivalent width increases less rapidly with u_2. It finally increases as $u_2^{\frac{1}{2}}$ when the absorption in the second cell dominates that in the first and when the absorption in the second cell can be represented by the strong line approximation.

In Fig. 2, $W/2\pi\alpha_1$ is shown as a function of qx_2/x_1 (which is proportional to u_2 along a given curve) when $x_1 = 1$. As u_2 increases and q is held constant the equivalent width first follows the uppermost limiting weak line curve (obtained by assuming that the absorption in the second cell can be described by the weak line approximation) until qx_2/x_1 is approximately 0.2q. Then the equivalent width increases less rapidly with u_2 until finally it increases as $u_2^{\frac{1}{2}}$.

When $x_1 = 100$, the first cell is in the strong line region. The variation of $W/2\pi\alpha_1$ as a function of qx_2/x_1 is shown in Fig. 3. The curves for constant q follow the upper limiting weak line curve until qx_2/x_1 is approximately 0.002. In this case the pressure in the second cell must be very much greater than that in the first cell in order for the second cell to make both a significant contribution to the absorption and to be in the weak line region.

In Figs. 4, 5, and 6 the quantity $W/2\pi\alpha_1$ is shown as a function of $\beta_2^2 x_2/\beta_1^2 x_1$ at constant q and x_1. In this plot the uppermost limiting curve is obtained when the absorption in the second cell can be described by the strong line approximation. In Fig. 4 where $x_1 = 0.01$, a curve at constant q approaches the uppermost limiting curve as x_2 increases and becomes virtually identical with it when $q^2 x_2/x_1$ is greater than $200q^2$. In this case when the pressure in the second cell is greater than in the first cell as, for example, the curve for $q = 10$, then the amount of absorbing gas in the second cell must be correspondingly large to have the total absorption vary as required by the strong line approximation.

In Fig. 5 for $x_1 = 1$, the curves approach the limiting strong line curve when $q^2 x_2/x_1$ is greater than $2q^2$. In Fig. 6 for $x_1 = 100$, the corresponding value for $q^2 x_2/x_1$ is $0.02q^2$. In this case it is necessary for the pressure in the second cell to be very much greater than that in the first cell before any deviations from the limiting strong line curve can be noticed.

III. Absorption by a Band

The effects due to the overlapping of spectral lines in a band are considered in this section. If we order and number the spectral lines of a band within the frequency interval $\Delta\nu$ with the index $\underline{i}$, we may write the absorption coefficient of the $\underline{i}$th spectral line as $k_j^{(i)}$ for the $\underline{j}$th absorption cell. The equivalent width is now

$$W = \int_{\Delta\nu} [1-\exp(-\Sigma\Sigma_{ij} k_j^{(i)} u_j)]d\nu, \tag{29}$$

where

$$[k_j^{(i)}(\nu,\nu_{oi},p_j,T_j) = S_j^{(i)} b_j^{(i)}(\nu,\nu_{oi},p_j,T_j)$$

$$= S_j^{(i)} \alpha_j^{(i)} \Big/ \{\pi[(\nu-\nu_{oi})^2 + \alpha_j^{(i)2}]\}. \tag{30}$$

The index i always refers to a particular spectral line, while the index j refers to a particular absorption cell.

A. General Results for a Band

1. Weak Line Approximation

If the weak line approximation is valid, the exponential in Eq. (29) can be replaced by the first two terms in its series expansion as in Section II. We obtain by the same procedure as given there that the equivalent width for the band is

$$W = \sum_j W_j , \tag{31}$$

where now W_j is the equivalent width for the band of radiation which passes through only the jth absorption cell so that

$$W_j = \int_{\Delta\nu} [1-\exp(-\sum_i k_j^{(i)} u_j)]d\nu. \tag{32}$$

This reduces to

$$W_j = u_j \sum_i S_j^{(i)}$$

when the weak line approximation is applicable and virtually all of the absorption occurs in the frequency interval $\Delta\nu$.

Thus, even for a band of overlapping lines the equivalent width is the sum of the equivalent widths of the radiation passing through the individual absorption cells provided only that the weak line approximation is valid. This result is true for any line shape, any degree of overlapping of the spectral lines, and any frequency interval $\Delta\nu$, even though some of

the absorption from these lines occurs outside of the interval $\Delta\nu$.

The required pressure p_h, temperature T_h, and amount of absorbing gas u_h for a homogeneous path through a single absorbing cell which has the same equivalent width as the series of individual absorption cells can easily be derived from these relations. When virtually all of the absorption occurs within the frequency interval $\Delta\nu$, the total equivalent width for the series of absorption cells is

$$W = \sum_j u_j \Sigma S_j^{(i)}. \tag{33}$$

If this result is compared with the similar expression for a single absorption cell, we obtain that

$$u_h \Sigma S_h^{(i)} = \sum_j u_j \Sigma S_j^{(i)} \tag{34}$$

where $S_h^{(i)}$ is the intensity of the ith spectral line at the temperature T_h of the single absorption cell with the homogeneous path.

When the temperature is the same in all of the various absorption cells, then Eq. (34) reduces to the very simply form

$$u_h = \sum_j u_j. \tag{35}$$

Eqs. (34) and (35) are the generalizations of the corresponding slant path Eqs. (14) and (15) as given by Plass[4].

2. Strong Line Approximation

When the spectral lines overlap appreciably, the derivation given in Section IIB can no longer be followed. Instead it is necessary to use the treatment given by Plass[4] which follows Eq. (17) of that article. If the variation of the half-width with pressure and temperature is given by

$$\alpha_j^{(i)} = \alpha_h^{(i)}(p_j/p_h)(T_h^{\frac{i}{2}}/T_j^{\frac{i}{2}}) \tag{36}$$

and it is assumed that the variation of the line strength with temperature can be represented by

$$S_j^{(i)} = S_h^{(i)} s(T_j), \tag{37}$$

where $s(T_j)$ is a function that can be calculated from the theory of molecular spectra, then we obtain

$$p_h T_h^{-\frac{i}{2}} u_h = \sum_j s(T_j) p_j T_j^{-\frac{i}{2}} u_j \tag{38}$$

or

$$S_h^{(i)} \alpha_h^{(i)} u_h = \sum_j S_j^{(i)} \alpha_j^{(i)} u_j, \tag{39}$$

where Eq. (39) is actually independent of the index $\underline{i}$ because of Eqs. (36) and (37). Equations (38) and (39) are valid for any variation of the line intensities, half-widths, and spacing between the lines in the finite spectral interval $\Delta\nu$, even though some of the absorption from these lines occurs outside of the interval $\Delta\nu$.

If all the spectral lines in the spectral interval $\Delta\nu$ have the same intensity S and the half-widths of the different spectral lines are equal, then Eq. (39) reduces to

$$S_h \alpha_h u_h = \sum_j S_j \alpha_j u_j, \tag{40}$$

where S_j and α_j may be different in the various absorbing cells because of temperature and pressure differences. The line spacing need not be constant for Eq. (40) to apply.

If the temperature is the same in the various absorbing cells, then $S_h^{(i)} = S_j^{(i)}$ and Eq. (39) reduces to

$$p_h u_h = \sum_j p_j u_j \tag{41}$$

or

$$\alpha_h u_h = \sum_j \alpha_j u_j \, , \tag{42}$$

Equations (38) to (42) are the generalizations of the slant path Eqs. (27), (23), and (28) given by Plass[4]. These equations are also valid for any variation of the line intensities, half-widths, and spacing between the lines in the finite spectral interval $\Delta\nu$.

B. Elsasser Model

The Elsasser model assumes that the band is composed of a series of evenly spaced spectral lines all of which have the same intensity[8]. When this model accurately represents an actual band, several interesting expressions can be derived for the absorption by several cells in series.

For the Elsasser model, the absorption coefficient may be written[8]

$$k_j = \frac{S_j}{d} \frac{\sinh\beta_j}{\cosh\beta_j - \cos z} \, , \tag{43}$$

where

$$z = (2\pi/d)\,(\nu - \nu_o),$$

where ν_o is the position of one of the line centers. Thus from Eq. (1), we have that the absorptance is

$$A = \frac{1}{2\pi} \int_{-\pi}^{\pi} \left[1 - \exp\left(-\sum_j \frac{\beta_j x_j \sinh\beta_j}{\cosh\beta_j - \cos z}\right)\right] dz \tag{44}$$

The exponential in Eq. (44) can be replaced by the first two terms in

its series expansion when the weak line approximation is valid. In this case we find after an elementary integration that

$$A = \sum_j \beta_j x_j = d^{-1} \sum_j S_j u_j. \tag{45}$$

Thus the absorptance is obtained by summing the absorptances of each absorbing cell as required by Eq. (7). Each term in the sum is the usual expression for the absorptance by an Elsasser band in a single cell[8,9].

When the strong line approximation is valid and $\beta < 0.3$, the hyperbolic functions in Eq. (44) can be replaced by the first term in their series expansion [8] and we find that

$$A = \phi[(\tfrac{1}{2}\sum_j \beta_j^2 x_j)^{\frac{1}{2}}] = \phi[(\pi/d)^{\frac{1}{2}}(\sum_j S_j \alpha_j u_j)^{\frac{1}{2}}], \tag{46}$$

where $\phi(x)$ is the error function integral defined after Eq. (17). Equation (46) can alternately be derived from Eq. (40) and the customary expression for the absorptance along a homogeneous path which is valid in the strong line region[8]

$$A = \phi[(\pi/d)^{\frac{1}{2}}(S_h \alpha_h u_h)^{\frac{1}{2}}]. \tag{47}$$

C. Statistical Model

The statistical model assumes that there is no correlation between the positions of the line centers. Any distribution of line intensities may be assumed. The absorptance A along a homogeneous path was originally calculated by Mayer[12] and Goody[13]. It has been shown[14] that the absorptance for the statistical model may be written in the convenient form

$$A = 1-[1-(\bar{W}_h/Nd)]^N, \tag{48}$$

where

$$\bar{W}_h = \int_0^\infty W_h P(S)dS,$$

$$W_h = \int_{\Delta\nu} [1-\exp(-k_h u_h)]d\nu,$$

N is the number of spectral lines in the spectral interval $\Delta\nu$, W_h is the equivalent width for a single isolated spectral line over the homogeneous path, and $P(S)dS$ is the probability of finding a spectral line of intensity S in the interval dS. When N is reasonably large, Eq. (48) is given approximately by[12-14]

$$A = 1-\exp(-\bar{W}_h/d). \tag{49}$$

These equations for the absorptance along a homogeneous path have been generalized by Plass[4], cf. Eqs. (53) to (55), to a slant path with a continuous variation of pressure and temperature. The generalization to the case of a series of absorption cells is given in this section.

In each of the cases just mentioned, the striking result is obtained that the absorptance for the statistical model can easily be obtained if the equivalent width of a single isolated spectral line is known for the appropriate conditions. The absorptance for a series of absorbing cells is obtained from the usual derivation for the statistical model[12, 13, 14, 4] as

$$A = 1-[1-(\bar{W}/Nd)]^N, \tag{50}$$

where

$$\bar{W} = \int_0^\infty \cdots \int_0^\infty W \prod_j P_j(S_j)dS_j, \tag{51}$$

the equivalent width W is given by Eq. (1), and $P_j(S_j)$ is the probability distribution for the line intensities in the jth absorption cell. If N is reasonably large, Eq. (50) may be written

$$A = 1-\exp(-\bar{W}/d). \tag{52}$$

It is assumed in the derivation of Eqs. (50) to (52) that the same absorbing gases are in all of the cells so that their line centers coincide.

On the other hand if there are different gases in the absorbing cells so that there is no correlation in the position of the line centers from one cell to another, then it is easily shown by the above derivation that the total transmittance is the product of the transmittance of the individual cells.

Any result for the equivalent width of a single isolated spectral line from Section II can be substituted into Eqs. (50) to (52) to obtain the absorptance of a band which obeys the statistical model. These equations are of great generality and are valid for any line shape, regardless of how the pressure, temperature, and absorber concentration vary from cell to cell.

In order to give some examples of these equations, let us first assume that all the spectral lines have the same intensity, so that $\bar{W} = W$ and the integrations over intensity do not have to be done. These equations are used in the quasi-random model of band absorption[15]. When the weak line approximation is valid, we have from Eqs. (7) and (50)

$$A = 1-\left[1-\left(\sum_j W_j/Nd\right)\right]^N \tag{53}$$

or if N is reasonably large

$$A = 1-\exp(-\Sigma_j W_j/d)$$
$$= 1-\prod_j \exp(-W_j/d) \qquad (54)$$

In this case the transmittance, τ is the product of the transmittances of the individual cells, so that $\tau = \prod_j \tau_j$. This is the expected result, since the arrangement of the spectral lines in the band is immaterial in the weak line approximation.

When the strong line approximation is valid in all of the absorption cells, then the absorptance can be obtained directly from Eq. (50) or (52) by the substitution of the appropriate expression for the equivalent width of a single isolated spectral line, Eq. (14), (15), (16), or (17). Similarly when the weak line approximation is valid for one of the absorption cells and the strong line approximation for another, then the equivalent width of a single line is obtained from Eq. (19) or (25) together with their approximations, Eqs. (23), (24), (27), and (28).

The case when the probability of finding a spectral line of intensity S in a given intensity range decreases approximately exponentially, so that

$$P(S) = S_o^{-1} \exp(-S/S_o), \qquad (55)$$

has been discussed extensively in the literature.[12,13,14] An exact expression for the absorptance can be calculated for this distribution. The result for a homogeneous path is[12,13,14]

$$A_h = \beta_h x_{oh}/(1+2x_{oh})^{\frac{1}{2}}, \qquad (56)$$

where

$$\beta = 2\pi\alpha/\Delta\nu$$
$$x_o = S_o u/2\pi\alpha,$$

the subscript h refers to the homogeneous path, and it is assumed that all of the absorption due to the spectral line occurs within the spectral interval $\Delta\nu$. Although the intensity distribution of most spectral bands is not accurately represented by Eq. (55), it is interesting to study this example since exact analytic expressions can be obtained for the absorptance in this case.

For two absorption cells in series, the absorptance is given by Eq. (50) where $\bar{W}$ as obtained from Eqs. (1), (51), and (55) is given by

$$\bar{W} = \Delta\nu - 2\int_0^{\frac{1}{2}} \frac{\Delta\nu}{\nu^2+\alpha_1^2+\pi^{-1}S_{o1}\alpha_1 u_1} \frac{\nu^2+\alpha_1^2}{\nu^2+\alpha_2^2+\pi^{-1}S_{o2}\alpha_2 u_2} d\nu \,. \tag{57}$$

This integral can be evaluated by writing each fraction in the integrand as unity minus another fraction. The resulting integrals can all be evaluated so that we find

$$\bar{W} = W_1 + W_2 - \frac{W_1 W_2}{\pi[\alpha_1(1+2x_{o1})^{\frac{1}{2}} + \alpha_2(1+2x_{o2})^{\frac{1}{2}}]} \,, \tag{58}$$

where

$$W_1 = 2\pi\alpha_1 x_{o1}/(1+2x_{o1})^{\frac{1}{2}} \tag{59}$$

and a corresponding expression for W_2.

It is interesting to compare this result with the equivalent width of a single line in the weak and strong line limits. When the absorption from both cells is described by the weak line approximation ($x_{o1} < 0.2$, $x_{o2} < 0.2$), then an expansion of Eq. (58) leads to Eq. (7). The equivalent width is still the sum of the individual equivalent widths regardless of the intensity distribution. On the other hand, when $x_{o1} > 2$ and $x_{o2} > 2$, then an expansion of Eq. (58) shows that in the strong line limit

$$\bar{W} = W_1 + W_2 - [W_1 W_2/(W_1+W_2)]. \qquad (60)$$

This does not agree with Eq. (15) since in this limit the distribution of line intensities can change the relationship between the values of W_j for each absorption cell and the total $\bar{W}$. The same type of result is obtained when the weak line approximation applies to one cell alone and the strong line approximation to the other.

IV. Interpolation Procedures

General results are derived in Section III which determine the amount of absorbing gas, the pressure, and the temperature for a homogeneous path through a single absorption cell whose total absorptance is equal to that of a number of absorption cells in series. The results for the weak line approximation, Eqs. (34) and (35), determine the required amount of absorbing gas, u_h, along the homogeneous path, but still allow an arbitrary choice for the pressure along this path. On the other hand, the results for the strong line approximation, Eqs. (39), (40), (41), and (42), determine the product $p_h u_h$ or $\alpha_h u_h$.

It is possible to satisfy simultaneously any pair of these weak and strong line equations since the weak line equation determines the value of u_h and the strong line equation can then be solved to find α_h or p_h. These results can then be substituted into any equation which has been derived for the absorptance of a homogeneous path in order to obtain the absorptance of a series of absorption cells. They can also be used equally well in connection with any experimental measurements or calculated tables of homogeneous path absorptance in order to determine the absorptance of a number of cells in series. The absorptance for a series of cells calculated in this manner must numericaly agree with the correct result when the absorptance

of each of the cells considered individually can be described by either the weak line or the strong line approximation. It might be expected that the resulting equations would also describe the absorption accurately in the intermediate region and in the case when the absorptance of one cell is best represented by the weak line approximation while another cell is best represented by the strong line approximation.

Equations derived by this same method have proved to be very useful for many atmospheric slant paths.[5,6,4] The actual atmospheric slant path can be considered to be the limit of a number of cells in series each with a different amount of absorber gas, pressure, and temperature. However, in the actual atmosphere the amount of absorber gas in each cell decreases as the pressure decreases provided that the absorber is uniformly distributed in the atmosphere. The situation is quite different in a laboratory experiment where the amount of absorbing gas and the pressure in each cell may have any arbitrary value within wide limits. Because of this fact the absorptance equations derived by the interpolation procedure must be used with care in the case of two or more cells in series.

As an example of the interpolation procedure assume that the line intensity and half-width of each line in the frequency interval $\Delta\nu$ are equal, so that $S_j = S_j^{(i)}$ and $\alpha_j = \alpha_j^{(i)}$. The equivalent path length and pressure for a homogeneous cell are then obtained by solving Eqs. (34) and (40) with the result that

$$u_h = S_h^{-1} \sum_j u_j S_j \tag{61}$$

and

$$\alpha_h = \frac{\sum_j S_j \alpha_j u_j}{\sum_j S_j u_j} \tag{62}$$

These equations are valid for both a single spectral line and for the Elsasser model, but are even more general than this since they are valid for any arbitrary variations of the spacing between lines in the spectrum. Equations (61) and (62) are also valid if the half width varies from line to line provided $\alpha_h^{(i)}$ and $\alpha_j^{(i)}$ are written for the half-widths in Eq. (62).

When the line intensities vary from line to line, but their temperature dependence can be represented by Eq. (37), then we find from Eqs. (34) and (39) that

$$S_h^{(i)} u_h = \sum_j S_j^{(i)} u_j \tag{63}$$

and

$$\alpha_h^{(i)} = \frac{\sum_j S_j^{(i)} \alpha_j^{(i)} u_j}{\sum_j S_j^{(i)} u_j} \tag{64}$$

Because of the assumptions made, the two quantities u_h and $\alpha_h^{(i)}/\alpha_j^{(i)}$ calculated from these equations are actually independent of i.

Finally when the temperature can be considered constant in the various cells, we find the quantity u_h from Eq. (35) and α_h from Eq. (41) as

$$\alpha_h \sum_j u_j = \sum_j \alpha_j u_j \tag{65}$$

The values of u_h and α_h from any appropriate pair of these equations can then be substituted into any suitable equation for band absorptance. For example, if the statistical model is valid, these values can be substituted into Eq. (48), (49), or (56).

In order to study the interpolation procedure let us consider the equivalent width of a single spectral line which for a homogeneous path is given by

$$W_h = 2\pi\alpha_h f(x_h), \tag{66}$$

where

$$x_h = S_h u_h / 2\pi\alpha_h$$

and

$$f(x) = xe^{-x}[I_o(x)+I_1(x)],$$

where I_o and I_1 are the Bessel functions of imaginary augument. If all the cells can be considered to be at constant temperature, then it follows from Eqs. (35), (65), and (66) that

$$W = \frac{2\pi\Sigma_j \alpha_j u_j}{\Sigma_j u_j} f\left[\frac{S(\Sigma_j u_j)^2}{2\pi\Sigma_j \alpha_j u_j}\right] \tag{67}$$

A comparison of this approximate equation was made with the previously calculated exact values for the equivalent width when there are two cells in series. Equation (67) gave an accurate representation of the equivalent width when both cells had values of u_j and α_j such that their absorptance could be represented individually by the weak line approximation. Similarly it provided an accurate representation when both cells could be represented by the strong line approximation. However, when one cell is represented by the weak line approximation and the other by the strong line approximation, then the interpolation procedure may or may not be a good approximation. It is a good approximation in this case only when almost all of the absorption occurs in one cell. When both cells contribute appreciably to the absorption, then the interpolation procedure may provide an inaccurate answer, as it does for the two cases illustrated in Figs. 7 and 8.

In Fig. 7, the equivalent width is shown as a function of x_2 when $x_1 = 0.01$ and $q = \alpha_2/\alpha_1 = 0.01$. The first cell can always be represented by the weak line approximation (because $x_1 = 0.01$) as can the second cell when $x_2 < 0.2$. In this region the interpolation procedure, Eq. (67), represents W accurately. When $x_2 > 200$, most of the absorption occurs in the second cell. For this reason Eq. (67) also accurately represents W even though the first cell is represented by the weak line approximation and the second by the strong line approximation. However, Eq. (67) fails to represent the actual absorption in the region $2 < x_2 < 200$ where the two cells are still represented by different approximations and where the absorption of radiation in each of the two cells is of the same order of magnitude.

A similar situation is shown in Fig. 8 where $x_1 = 100$ and $q = \alpha_2/\alpha_1 = 100$. The interpolation procedure, Eq. (67), fails when $0.002 < x_2 < 1$. In this region again both cells make the same order of magnitude contribution to the absorption while the first cell can be represented by the strong line approximation and the second by the weak line approximation.

For comparison, Eq. (7) is also plotted in Figs. 7 and 8. This equation assumes that both cells can be represented by the weak line approximation. In Fig. 7 it agrees with the correct value when $x_2 < 0.2$, as would be expected. It is not valid for any of the values shown in Fig. 8, since with $x_1 = 100$ this first cell can never be represented by the weak line approximation.

Equation (15) is also plotted in these figures. This equation assumes that both cells can be represented by the strong line approximation. This is true in Fig. 8 when $x_2 > 2$ and it does provide a good representation in

this region. In Fig. 7, Eq. (15) also provides a good representation when $x_2 > 200$. Although the first cell cannot be represented by the strong line approximation in this case, nevertheless Eq. (15) can be used when $x_2 > 200$ since virtually all of the absorption occurs in the second cell in this region.

V. Conclusions

The equivalent width of an isolated spectral line or of a band of non-overlapping lines is derived in Section II. It is shown that the equivalent width is the sum of the equivalent widths of each absorbing cell in the path of the radiation, Eq. (7), when the weak line approximation describes the absorption in each cell considered individually. When the strong line approximation is applicable to each cell, the equivalent width is given by the square root of the sum of the squares of the individual equivalent widths of each cell, Eq. (15). When the absorption of one cell is described by the weak line approximation and that of a second cell by the strong line approximation, the equivalent width can be obtained from Eq. (19) or (25). Illustrative examples are given for all of these cases.

The absorptance of a spectral band composed of overlapping spectral lines is considered in Section III. First an equivalent amount of absorbing gas, pressure, and temperature are obtained for a homogeneous path which has the same absorptance as the actual path through two or more cells in series. The weak line result is given by Eqs. (33) and (34) and the strong line result by Eqs. (39), (40), (41), and (42). The absorptance for a series of cells is derived when the Elsasser model is valid, Eqs. (44), (45), and (46), and when the statistical model is valid, Eqs. (50), (52), (53), (54), and (58) together with Eqs. (14), (15), (16), and (17).

The interpolation procedure is studied in Section IV. An equivalent pressure and amount of absorbing gas is calculated by satisfying simultaneously both the weak and strong line equations. This procedure provides useful simplified expressions for the absorptance when the absorption by all of the individual cells can be represented by either the weak line or by the strong line approximation. However the results are inaccurate when both of these conditions are satisfied: (1) the absorption by some of the cells is represented by the weak line approximation, while other cells are represented by the strong line approximation; (2) each of the groups of cells makes a significant contribution to the absorption of the radiation.

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Legends for Figures

Fig. 1. The equivalent width W for a single spectral line absorbed by two cells in series as a function of $1+(S_2u_2/S_1u_1)$. S_1, u_1, α_1 are the line intensity, amount of absorbing gas, and half-width in the first cell and S_2, u_2, α_2 are the same quantities in the second cell. The uppermost curve is the weak line limit, which assumes that the absorption by the second cell can be represented by the weak line approximation. These curves are for $x_1 = S_1u_1/2\pi\alpha_1 = 0.01$ and for various values of $q = \alpha_2/\alpha_1$.

Fig. 2. The equivalent width W for a single spectral line absorbed by two cells in series as a function of S_2u_2/s_1u_1. These curves are for $x_1 = 1$ and various values of q.

Fig. 3. The equivalent width W for a single spectral line absorbed by two cells in series as a function of S_2u2/S_1u_1. These curves are for $x_1 = 100$ and various values of q.

Fig. 4. The equivalent width W for a single spectral line absorbed by two cells in series as a function of $S_2\alpha_2u_2/S_1\alpha_1u_1$. The uppermost curve is the strong line limit which assumes that the absorption by the second cell can be represented by the strong line approximation. These curves are for $x_1 = 0.01$ and various values of q.

Fig. 5. The equivalent width W for a single spectral line absorbed by two cells in series as a function of $S_2\alpha_2u_2/S_1\alpha_1u_1$. These curves are for $x_1 = 1$ and various values of q.

Fig. 6. The equivalent width W for a single spectral line absorbed by two cells in series as a function of $S_2\alpha_2u_2/S_1\alpha_1u_1$. These curves are for $x_1 = 100$ and various values of q.

Fig. 7. The equivalent width W for a single spectral line absorbed by two cells in series as a function of x_2 when $x_1 = 0.01$ and $q = 0.01$. On the scale of this figure the actual value and that obtained from the approximate Eq. (19) cannot be distinguished. The results obtained from various approximate equations are also shown: interpolation procedure, Eq. (67); weak line approximation, Eq. (7); strong line approximation, Eq. (15).

Fig. 8. The equivalent width W for a single spectral line absorbed by two cells in series as a function of x_2 where $x_1 = 100$ and $q = 100$. On the scale of this figure the actual value and that obtained from the approximate Eq. (19) cannot be distinguished. The results obtained from various approximate equations are also shown: interpolation procedure, Eq. (67); weak line approximation, Eq. (7); strong line approximation, Eq. (15).

W/2πa1 ⟶
10·0
1·0
0·1
1
10
100
1000
10,000
100,000
1
⟵ (1 + (S2 u2 / S1 u1)
WEAK LINE LIMIT
q = 10
q = 1
q = 0·1
q = 0·01
q = 0·001
X1 = 10·0
a1/a2 = q

W/2πα1 →
0.1
1
10
100
10.0
1.0
0.1
0.01
0.001
0.0001
← 1n1S/2n2S
α2/α1=b
X1=1
WEAK LINE LIMIT
q=100
q=10
q=1
q=0.1
q=0.01

W / 2π a1 ⟶
1
10
100
1000
10.0
1.0
.1
.01
.001
.0001
⟵ ln 1 S1/S2 u2 S2
X1 = 100
a1/a2 = a2b
WEAK LINE LIMIT
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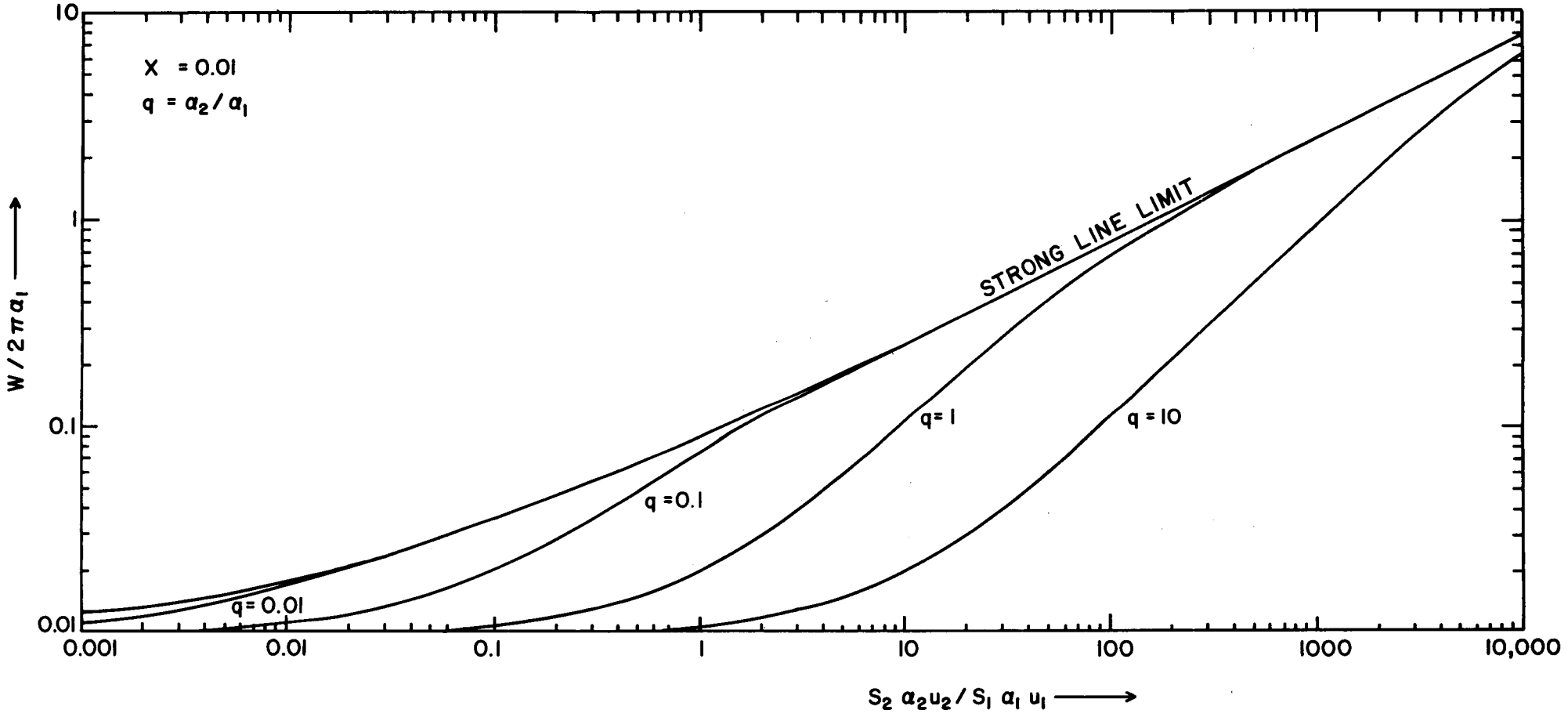
b = 1.0
b = .1
b = .01
b = .001
b = .0001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q = α2 / α1
STRONG LINE LIMIT
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q = 10
q = 0.1
q = 0.01
W / 2π α1
S2 α2 u2 / S1 α1 u1
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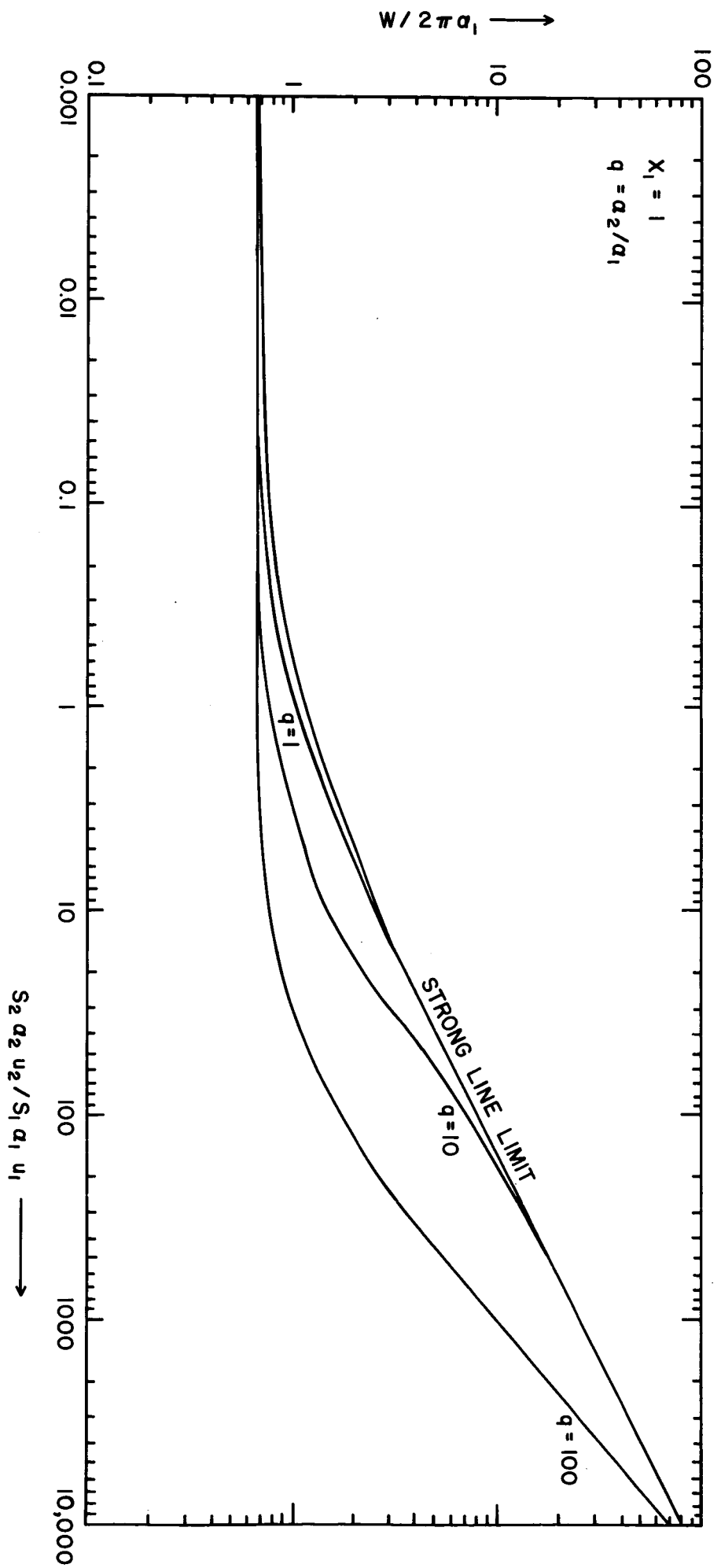
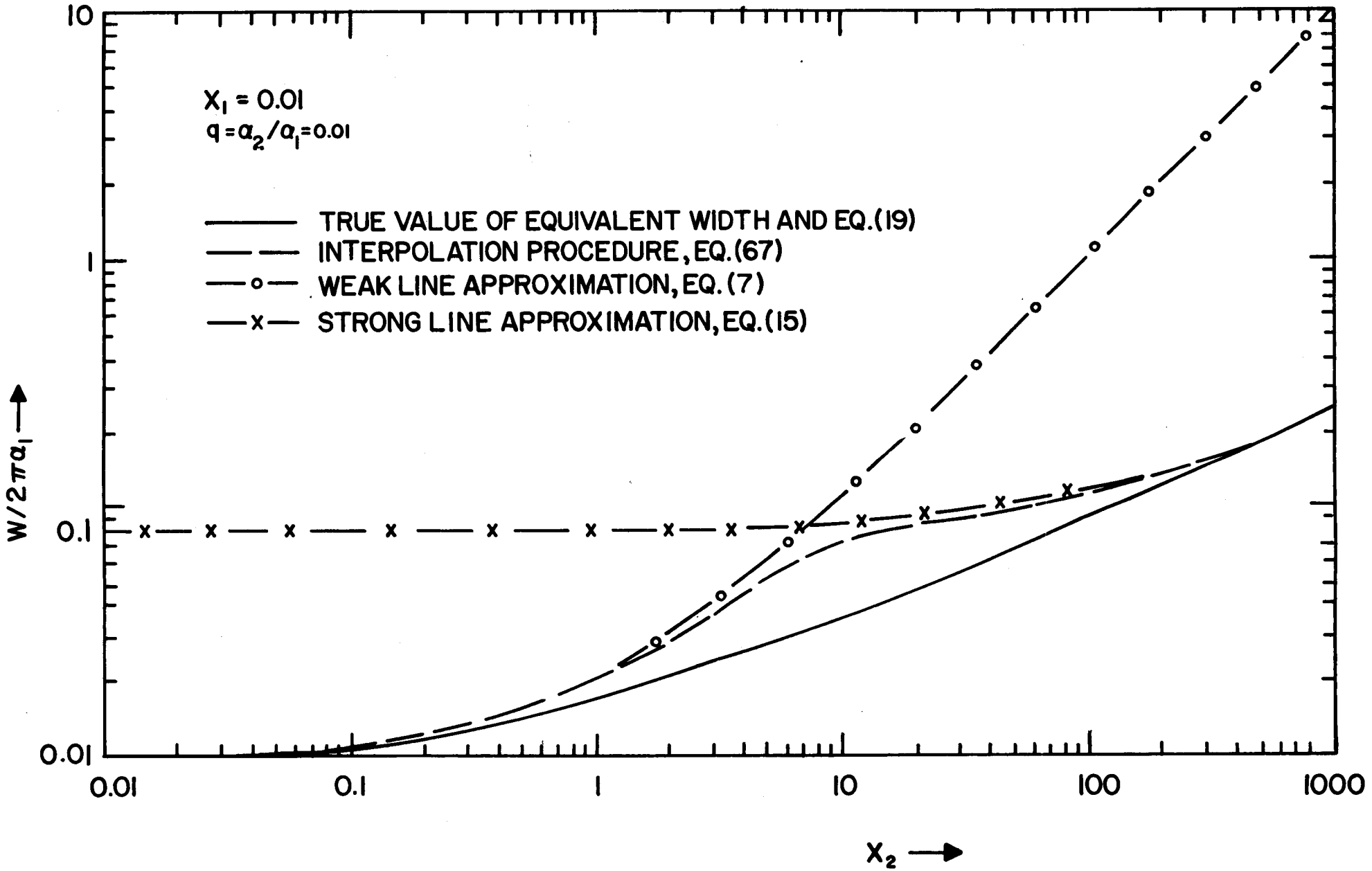
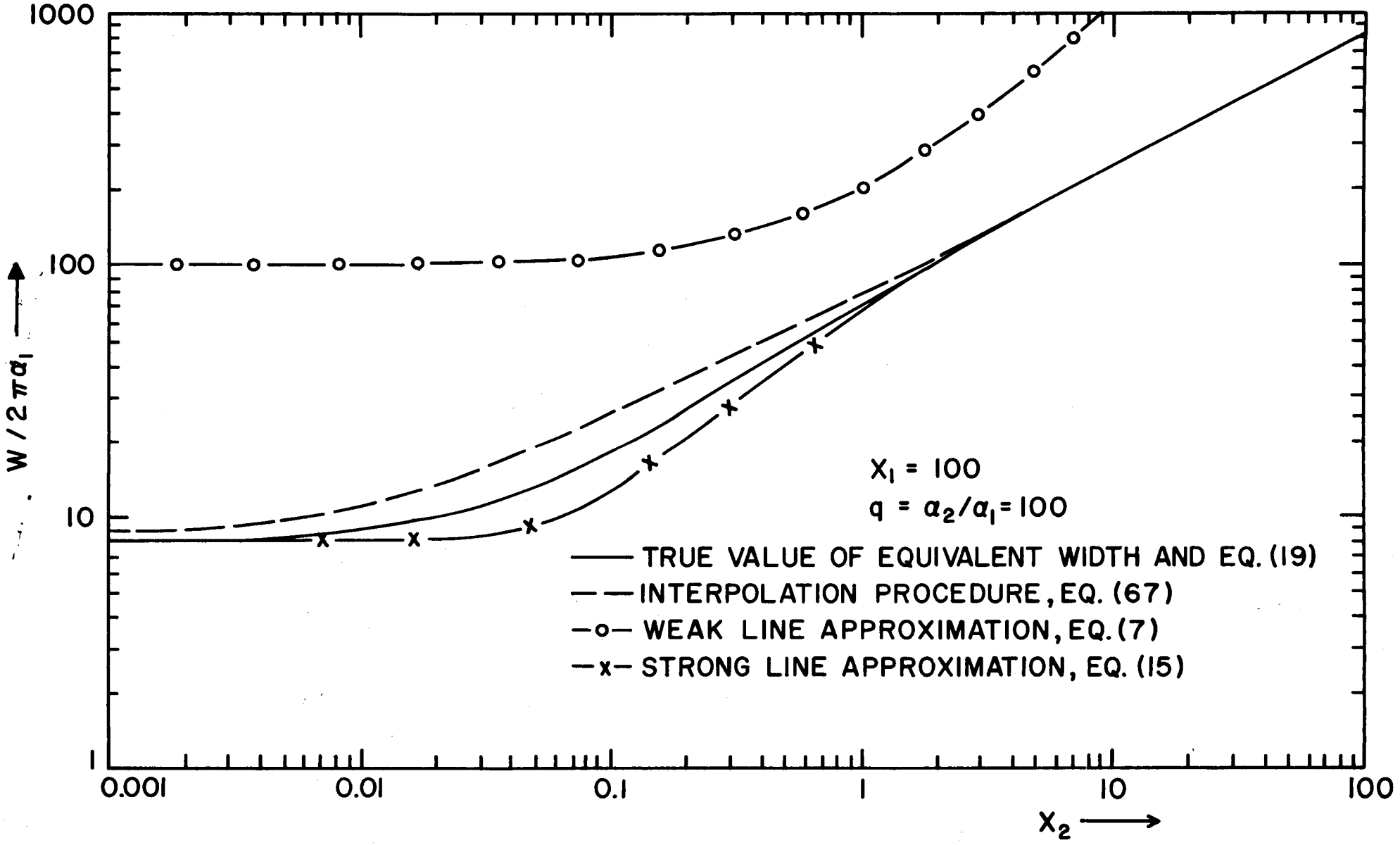
1
0.1
0.01
0.001
0.01
0.1
1
10
100
1000
10,000


W / 2π a1 ⟶
0.1
1
10
100
0.001
0.01
0.1
1
10
100
1000
10,000
S2 a2 u2 / S1 a1 u1 ⟶
q = a2/a1
X1 = 1
q=1
q=10
q=100
STRONG LINE LIMIT

W/2πa1 →
1000
100
10
1
.1
.01
.001
.0001
10,000
1,000
100
10
1
.1
.01
← S2a2u2/S1a1u1
q=.001
q=.01
q=.1
STRONG LINE LIMIT
X1 = .01
q=a2/a1


$X_1 = 0.01$
$q = \alpha_2/\alpha_1 = 0.01$
TRUE VALUE OF EQUIVALENT WIDTH AND EQ.(19)
INTERPOLATION PROCEDURE, EQ.(67)
WEAK LINE APPROXIMATION, EQ.(7)
STRONG LINE APPROXIMATION, EQ.(15)
$W/2\pi\alpha_1$
X_2
10
1
0.1
0.01
0.01
0.1
1
10
100
1000


1000
100
10
1
W / 2πα1
0.001
0.01
0.1
1
10
100
X2
X1 = 100
q = α2/α1 = 100
TRUE VALUE OF EQUIVALENT WIDTH AND EQ. (19)
INTERPOLATION PROCEDURE, EQ. (67)
WEAK LINE APPROXIMATION, EQ. (7)
STRONG LINE APPROXIMATION, EQ. (15)